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(54) Title: CROSSLINKING OF RUBBERS WITH ENGINEERING PLASTICS (57) Abstract A process for the cross-linking of a polymer composition which comprises a thermoplastic crystalline or amorphous (co)polymer comprising repeating units containing at least one amide group and 10-90 parts by weight, based on the amount of amide (co)polymer, of an unsaturated natural or synthetic rubber, is disclosed. The process is characterized by the choice of a specific, high temperature C-C initiator which leads to improved properties in the cross-linked polymer blend. In addition, the use of a high temperature C-C initiator to cross-link a polymer composition which comprises a thermoplastic crystalline or amorphous (co)polymer comprising repeating units containing at least one amide group and 10-90 parts by weight, based on the amount of amide (co)polymer, of an unsaturated natural or synthetic rubber, is also disclosed.		

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Crosslinking of Rubbers with Engineering Plastics

5 The present invention relates to a process for the crosslinking of rubbers blended with engineering plastics and the products of that process. More particularly, the present invention relates to a process for the crosslinking of blends comprising at least one amide-containing polymer and at least one unsaturated rubber.

10 Thermoplastic elastomeric blends which comprise a continuous thermoplastic polymer and a dispersed crosslinked rubber can be prepared by the so-called dynamic crosslinking process, wherein the rubber is crosslinked during mixing with the thermoplastic polymer. The temperature used in the dynamic crosslinking process must be above the melting temperature of the thermoplastic polymer to ensure
15 sufficient mixing. Conventional crosslinking agents known to be effective for the rubber employed in the blend, may be used in such a process. Several examples of such processes can be found in the prior art.

20 J5 9109-539 discloses the vulcanization of a blend of polyamide resin, diene or olefin rubber, liquid diene rubber and a vulcanizing agent. As vulcanizing agents are disclosed organic peroxides and sulfur. Similarly, J5 9049-246 discloses blends of polyamide and acrylonitrile/butadiene rubber which are crosslinked with sulfur,
25 organic peroxides or maleimides. Further, DE 34 09 414 relates to the same blends of polyamide with acrylonitrile/butadiene rubber which are crosslinked with sulfur or maleimides.

30 J5 8206-667 relates to polyamide blends with ethylene/propylene/diene (EPDM) which are crosslinked with organic peroxides. Similarly, J0 2115-264 relates to blends of polyamide with nitrile rubber which can be crosslinked with sulfur, organic peroxides or maleimides. Finally, GB 2,208,868 relates to blends of polyamide with nitrile rubber and

acrylic rubber wherein sulfur or organic peroxides may be used as the crosslinking agents.

5 However, when engineering plastics having a high melting point are employed in blends with rubbers, conventional crosslinking systems such as sulfur and peroxide curing systems are often unsuitable because at such temperatures the crosslinking reaction will be too rapid, thus impairing the mixing of the rubber and engineering plastic. In this case, other curing systems may be used.

10 For example, U.S. Patent 4,173,556 suggests the use of phenolic resin, peroxide, azide, quinoid or accelerated sulfur vulcanization systems for crosslinking blends of polyamides with rubbers. The use of a phenylene bismaleimide coagent is also recommended. U.S. patent 15 5,003,003 discloses the curing of a polyolefin containing a functionalized EPM or EPDM in a blend with polyamide. As curing agents are mentioned peroxides, sulfur, phenolics and reactive crosslinks with, for example functional groups such as epoxide, amine, alcohol or carboxylic acid which are attached to the EPM or EPDM.

20 Also, European Patent Application 382 539 discloses the crosslinking of polyamide blends with ethylene polymers using hexamethylenediamine carbamate as the crosslinking agent. Finally, U.S. patent 4,501,841 25 discloses the curing of aramide blends with EPDM wherein the curing agent is a peroxide.

30 While these crosslinking systems do not suffer from the disadvantage that they crosslink too rapidly when working with high-melting engineering plastics, as do the peroxides, these systems are not ideal crosslinking systems. This factor severely limits the possible products and uses which can be obtained from blending polyamides with engineering plastics.

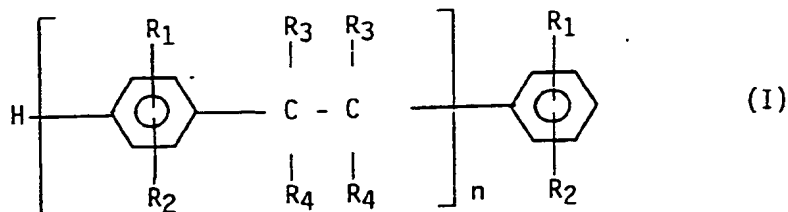
Accordingly, the goal of the present invention is to provide a novel crosslinking process for crosslinking blends of polyamides with engineering plastics, which process eliminates the disadvantages of the prior art processes and thereby leads to blends exhibiting improved properties.

A further object of the present invention is to provide a crosslinking process for blends of polyamides and engineering plastics, which process provides more flexibility than prior art processes allowing the man of skill to tailor his process to the particular type of product that he wishes to produce.

These and other objects of the present invention will be apparent to the man of skill in the art from the Summary and Detailed Description of the Invention which follow.

Summary of the Invention

The present invention relates to a process for the cross-linking of a polymer composition which comprises a thermoplastic crystalline or amorphous (co)polymer comprising repeating units containing at least one amide group and 10-90 parts by weight, based on the amount of amide (co)polymer, of an unsaturated natural or synthetic rubber, characterized in that said polymer composition is heated to a temperature above the melting point of said amide (co)polymer and an initiator selected from oligomers of triisopropyl benzene, 1-isopropylnaphthalene dimer, 2-isopropylnaphthalene dimer and initiators represented by the formula i:



wherein R_1 and R_2 are independently selected from hydrogen, linear or branched C_1 - C_{10} alkyl and C_2 - C_{10} alkenyl groups, which may be optionally substituted with one or more halogen atoms, chlorine, $-C-O-R$ and $-C(O)OR$; wherein R is a hydrogen, or C_1 - C_{10} alkyl group;

R_3 and R_4 are independently selected from, $-C\equiv N$, $-COOH$, $-O-CH_3$, $-OH$, and linear or branched C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl and aryl groups, which may be optionally substituted with one or more halogen atoms, chlorine, $-C-O-R$ and $-C(O)OR$; wherein R is a C_1 - C_{10} alkyl group; and $n=1-100$; is added with mixing to the heated polymer composition to thereby crosslink the polymer composition.

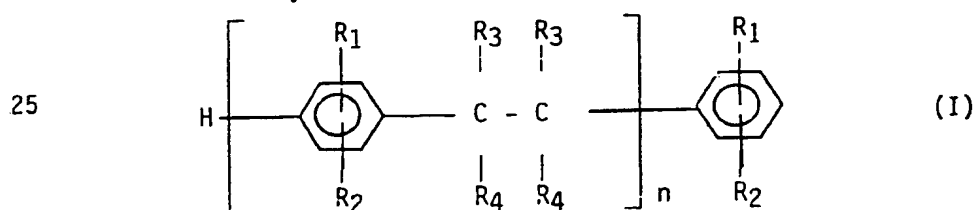
In addition, the present invention relates to the use of an initiator selected from oligomers of triisopropyl benzene, 1-isopropylnaphthalene dimer, 2-isopropylnaphthalene dimer and initiators represented by the formula I to cross-link a polymer composition which comprises a thermoplastic crystalline or amorphous (co)polymer comprising repeating units containing at least one amide group and 10-90 parts by weight, based on the amount of amide (co)polymer, of an unsaturated natural or synthetic rubber; by addition of said initiator to said polymer composition at a temperature above the melting point of said amide (co)polymer.

The process and use of the present invention provide advantageous properties in the polymer blends which are produced by the process. For example, it is possible to improve the tensile strength of the blends with the present process. It is also possible to tailor the

blends using the process of the present invention since the improvement in properties resulting from the process can compensate for the adverse effects of antioxidants or polymer plasticizers which can be added to improve other properties. Further, in many cases other properties of the polymer blend are improved by the process of the present invention, including flow, heat stability and Shore D hardness, for example.

Detailed Description of the Invention

The present invention relates to a process for the cross-linking of a polymer composition which comprises a thermoplastic crystalline or amorphous (co)polymer comprising repeating units containing at least one amide group and 10-90 parts by weight, based on the amount of amide (co)polymer, of an unsaturated natural or synthetic rubber, characterized in that said polymer composition is heated to a temperature above the melting point of said amide (co)polymer and an initiator selected from oligomers of triisopropyl benzene, 1-isopropylnaphthalene dimer, 2-isopropylnaphthalene dimer and initiators represented by the formula I:



wherein R₁ and R₂ are independently selected from hydrogen, linear or branched C₁-C₁₀ alkyl and C₂-C₁₀ alkenyl groups, which may be optionally substituted with one or more halogen atoms, chlorine, -C-O-R and -C(O)OR; wherein R is hydrogen or a C₁-C₁₀ alkyl group;

5 R₃ and R₄ are independently selected from linear or branched C₁-C₁₀ alkyl and C₂-C₁₀ alkenyl groups, which may be optionally substituted with one or more halogen atoms, chlorine, -C-O-R and -C(O)OR; wherein R is a C₁-C₁₀ alkyl group; and n=1-100; is added with mixing to said heated polymer composition to thereby crosslink the polymer composition.

10 Preferred initiators of the formula I are 2,3-dimethyl-2,3-diphenylbutane, 3,4-dimethyl-3,4-diphenylhexane, 3,4-diethyl-3,4-diphenylhexane, 1,2-dihydroxy-1,1,2,2-tetraphenylethane, 1,2-dicyano-1,2-dicarboxy-1,2-diphenylethane, 1,2-dicyano-1,2-dimethoxy-1,2-diphenylethane, and oligomers of diisopropylbenzene.

15 Many of the compounds of the formula I are known as high temperature initiators from, for example, "Untersuchungen zur Verwendung eines neuen peroxidfreien Initiators vom Dibenzyltyp bei der Heißhärtung von UP-Harzen," Wolfers, H., et al. Kunststoffe 68, Vol. 9, pp. 553-555 (1978). In this publication the disclosed use of the initiators is
20 the curing of unsaturated polyester resins.

25 Some of the initiators employed in the process of the present invention can also be found in U.S. patent 3,125,546. Here the initiators are employed for the crosslinking of vinyl chloride polymers with diallyl monomers and a peroxide catalyst.

30 Also, Japanese patent application JO 2123-164 published on 2 November 1988 discloses the use of an initiator in accordance with the formula I (Perkadox 30) for the curing of a blend of rubber with polypropylene or polyethylene. However, this publication does not mention blends of rubbers with amide-containing polymers nor does it suggest the advantages of the present initiators when used in the process of the present invention.

Suitable rubbers for use in the blends crosslinked by the process of the present invention comprise unsaturated rubbers. More particularly, the following rubbers are preferred for use in the blends: poly(butadiene), poly(isoprene), natural rubber, poly(cyclopentadiene), poly(methylcyclopentadiene), polychloroprene, partly dehydro-chlorinated poly(vinyl chloride), butadiene/styrene copolymer, butadiene/acrylonitrile copolymer, partly hydrogenated butadiene/acrylonitrile copolymer, isoprene/styrene copolymer, isobutylene/isoprene copolymer, acrylonitrile/butadiene/styrene terpolymer, ethylene/propylene/diene terpolymer, isoprene/styrene/acrylonitrile terpolymer, rubbery, non-crystalline copolymers of butadiene or isoprene, mixtures of two or more of these rubbers and mixtures of these rubbers with one or more saturated rubbers.

The preferred rubbers for use in the process of the present invention are nitrile rubbers such as butadiene/acrylonitrile copolymers and partially hydrogenated butadiene/acrylonitrile copolymers. Such nitrile rubbers prepared with 15-60 weight percent, based on the total weight of the rubber, of acrylonitrile, are most preferred.

Suitable amide-containing polymers for use in the blends crosslinked by the process of the present invention comprise thermoplastic, crystalline or amorphous (co)polymers having repeating units containing amide groups.

More particularly, said amide-containing (co)polymer is selected from polycaprolactam (nylon-6), polyhexamethylene-1,4-butyrimide (nylon-4,6), polyhexamethylenedipamide (nylon-6,6), polyhexamethyleneazelaamide (nylon-6,9), polyhexamethylenesebacamide (nylon-6,10), polyhexamethyleneisophthalamide, polylauryllactam (nylon-12), the polyamide derivative of 11-aminoundecanoic acid and mixtures thereof.

The most preferred amide-containing polymers for use in the process of the present invention are crystalline polyamides having a melting point above 160°C.

5 The blends of the present invention comprise the amide-containing polymer and 10-90 parts by weight, based on the amide-containing polymer, of the unsaturated rubber. More preferably, the blends contain 30-70 parts by weight, based on the amide-containing polymer, of unsaturated rubber.

10 The crosslinking process of the present invention is carried out at a temperature above the melting point of the amide-containing polymer. The temperature must also be sufficiently high to cause decomposition of the initiator. However, the temperature should be maintained as low as possible while satisfying the above two conditions in order to avoid unnecessary thermal degradation of the (co)polymers, which degradation will depend, to a large extent, on the type of (co)polymers employed, as well as the presence or absence of antidegradants.

20 Suitable reaction temperatures are in the range of 160-300°C, and more preferably from 200-270°C. Suitable reaction times are strongly dependent upon the degree of crosslinking desired, the polymer blend, the particular initiator employed and the reaction temperature. However, generally the reaction time is in the range of 5 seconds to 15 minutes and more preferably lasts from 15 seconds to 5 minutes. Once crosslinked, the polymer blend may be shaped into the desired article.

30 The polymer blend is first heated to a temperature above the melting point of the amide (co)polymer and then the initiator is added to the heated polymer blend.

It is preferred to mix the polymer blend and the initiator thoroughly during the crosslinking process. Mixing can be carried out in a batch or continuous process, for example in an internal mixer, a mixing extruder or a kneader.

5 The amount of initiator employed in the present process should be chosen to provide an amount sufficient to achieve the desired degree of crosslinking. The amount of initiator will have to be adjusted on the basis of the type of rubber employed. Generally, 0.1 to 10 weight
10 parts of initiator, based on the weight of the rubber, is sufficient. More preferably, 0.5 to 5.0 weight parts of initiator, based on the weight of the rubber, are employed.

15 In a particularly preferred embodiment of the process of the present invention, crosslinking coagents are employed in combination with the initiator. These crosslinking coagents lead to higher crosslink density and improvements in some of the properties of the blends. Particular types and amounts of crosslinking coagents can be chosen to tailor a particular blend to a particular application.

20 Typical crosslinking coagents are polyunsaturated crosslinking compounds. More particularly, crosslinking coagents such as allyl, styryl, isopropenylbenzene, methyl(meth)acrylate or maleimide-type coagents are preferably employed. Specific examples of crosslinking
25 coagents include: triallylcyanurate, triallylisocyanurate, divinylbenzene, diisopropenylbenzene, oligomers of diisopropenylbenzene, trimethylolpropane trimethacrylate, ethyleneglycol dimethacrylate and m-phenylene bismaleimide.

30 The amount of crosslinking coagent employed will depend upon the required amount of additional crosslinking which is desired. Generally, the amount of crosslinking coagent used will be from 0.1 to 5.0 parts by weight, based on the weight of the rubber.

Other optional ingredients may be present in the process of the present invention. These ingredients can be used to tailor particular products to particular applications, for example, or to prevent unnecessary degradation of the polymer blends under crosslinking conditions.

Optional ingredients include thermoplastic polymers other than those mentioned above, such as saturated rubbers, for example; fillers such as carbon black, silica, clay, whiting and other mineral fillers; plasticizers, process oils, extender oils, tackifiers, waxes; antidegradants such as stabilizers, antioxidants and antiozonants; adhesion promoters for promoting adhesion between fillers and substrates, and flame retardants. These are all conventional materials and the amounts employed as well as the means of addition to the crosslinking process are conventional for rubber crosslinking.

The present invention also encompasses the use of the initiators of the formula I in the above-described process.

The following examples are presented to illustrate and further describe the present invention. They are not to be construed as limiting the invention in any way. The scope of the invention is to be determined from the claims appended hereto.

Materials and Methods Used in the Performance of the Examples

Polymers

Krynac[®] 2980; ex. Polysar, Nitrile Rubber (NBR), (Acrylonitrile content of 29%).

Krynac[®] 5075; ex. Polysar, Nitrile Rubber (NBR), (Acrylonitrile content of 50%).

Akulon[®] M-258; High Viscosity; ex. Akzo, (Polyamide-6).
Akulon[®] K-136; Medium Viscosity; ex. Akzo, (Polyamide-6).
Akulon[®] M 223-D; Low Viscosity; ex. Akzo, (Polyamide-6).
Akulon[®] K-124; Low Viscosity; ex. Akzo, (Polyamide-6).
5 Akulon[®] S 223-E; ex. Akzo, (Polyamide-6,6).

Vestamid[®] L 1600; ex. C.W. Huls, (Polyamide-12).
Buna[®] CB-10; ex. C.W. Huls, Butadiene Rubber (BR).
Luran[®] 358N; ex. BASF, styrene/acrylonitrile copolymer (SAN).

10

Initiators

15 Perkadox[®] 30; ex. Akzo Chemicals; assay 95%
2,3-dimethyl-2,3-diphenylbutane, (Px30).
Oligomer of diisopropylbenzene (oligomeric Px30).

20 Perkadox[®] 58; ex. Akzo Chemicals; assay 95%
3,4-dimethyl-3,4-diphenylhexane, (Px58).

Trigonox[®] 101; ex. Akzo Chemicals; assay 90%
2,5-dimethyl-2,5-bis(tertiary butylperoxy) hexane, (Tx 101).

25 HVA-2[®]; ex. DuPont, m-phenylenebismaleimide.

SP 1045; phenolic curing agent.

Crosslinking Coagents

30 Perkalink[®] 300; ex. Akzo Chemicals; triallylcyanurate (TAC).

Oligomeric meta-diisopropenylbenzene; ex. Akzo Chemicals; (m-DIPB).

HVA-2[®]; ex. DuPont, m-phenylenebismaleimide.

Antioxidants

5 Permanax[®] TQ; ex. Akzo Chemicals; polymerized
1,2-dihydro-2,2,4-trimethylquinoline.

Permanax[®] 6PPD; ex. Akzo Chemicals;
N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine.
10 Weston 618[®], ex. Borg-Warner.

Plasticizers

Diethylphthalate (DOP);
15 Ketjenflex[®] 8 (KF 8), ex. Akzo Chemicals

Dynamic Cross-Linking Reaction

20 Rubber and amide-containing polymers were dynamically crosslinked in
the presence of the initiator using a Haake Rheocord[®] System 40 fitted
with a mixing chamber (Rheomix[®] 600) containing roller rotors. The
procedure used was blending the rubber and amide-containing polymer
for 3 minutes in the mixing chamber at 260°C. Then the initiator was
added and mixing was continued for an additional 10 minutes. The
25 reaction product was granulated and hot-pressed into a 1 mm. thick
sheet by compression molding.

The hot-pressing was carried out by using a 200 x 120 x 1 mm. mold
which was filled with the granulated blend and pressed at 260°C with
the following program:

- 30
1. Pressureless for 1 minute.
 2. 1 minute at 50 kN.
 3. 1 minute at 150 kN.
 4. 1 minute cold at 150 kN.

A mold release agent was used to enhance mold release. The 1 mm thick sheets were stored at room temperature.

5 In the tables which follow, the amount of initiator is expressed as weight parts (wt. pts.) or parts per hundred (phr), based on the total weight of polymer blend (rubber plus amide-containing polymer). In the experiments with PA-12 and PA-6,6, the reaction temperatures used were 240°C and 280°C, respectively, and instead of a 10 minute mixing period, mixing was continued for 15 and 5 minutes, respectively.

10

Test Procedures

15 All tests were carried out within one week after preparation of the one millimeter thick sheets, unless otherwise specified. Tensile tests were carried out one day after pressing the one millimeter thick sheets, unless otherwise specified.

The following test apparatus were employed:

20 Tensile Tests - Zwick® Tensile Tester 1445, (DIN 53504).

Tear Strength - Zwick® Tensile Tester 1445, (DIN 53515).

25 Viscosity Measurements - Göttfert® Rheograph 2001: capillary rheometer, T=260°C.

Vicat Softening Temperature - (DIN 53460: method A, 120°C/hour, 9.81N).

30 Compression Set - (DIN 53517A: 72 hours, 23°C).

Hardness (Shore D, DIN 53505).

Melt Volume Index (MVI) measurements were carried out at 260°C and 10 kg. load (Göttfert® Melt Indexer MP-E, (DIN 53735 and ASTM 1238).

Examples 1-3 and Comparative Examples A-D

High temperature dynamic cross-linking of NBR/PA blends: comparison of different XL agents

The composition and results of the dynamically cross-linked NBR/PA (60:40) blends in the mixing chamber are given in Table 1.

A C-C initiator (Px-30) was compared with a peroxide (Tx-101), a bismaleimide (HVA-2®) and a phenolic resin curing agent (SP 1045) in the dynamic cross-linking of an NBR/PA blend.

TABLE 1

	Example (wt.pts)						
	A	B	C	D	1	2	3
NBR (Krynac® 2980)	60	60	60	60	60	60	60
PA-6 (Akulon® K-136)	40	40	40	40	40	40	40
Tx 101	--	1	--	--	--	--	--
SP 1045	--	--	1	--	--	--	--
HVA-2®	--	--	--	1	--	--	--
Px 30	--	--	--	--	1	2	4
Properties							
Tensile Strength (dried) [MPa]	6.0	15.2	15.6	15.0	21.2	24.2	18.6
Tensile Strength (conditioned) [MPa]	6.0	15.7	14.9	14.4	21.2	22.3	19.3

The compounds dynamically cross-linked with Px-30 (1-2 phr) show substantially better tensile strength values than those cross-linked with Tx 101, HVA-2® and SP 1045.

The non-cross-linked control showed low tensile values. Tensile values obtained after 1 week conditioning at 23°C, 60% RH were quite similar to those obtained with dried samples (overnight-110°C vacuum).

5 Example 4 and Comparative Example E

Table 2 shows that NBR/PA dynamically cross-linked with Px 30 gave a thermoplastic material with better properties than the control without Px 30.

10

TABLE 2

Compound (wt.pts)	Example Number	
	E	4
NBR (Krynac® 2980)	60	60
PA-6 (Akulon® K-136)	40	40
Px 30	--	2
Properties		
Tensile Strength (MPa)	9	29
Elongation at break (%)	87	139
Modulus 5% (MPa)	3	7
10%	4	9
50%	7	14
Tear Strength (N/mm)	4	5
Compression Set (%)	60	64
Shore D Hardness	42	54
Vicat A °C	168	>200
Viscosity at shear (10 1/s)	14000	5800
Viscosity at shear (100 1/s)	1900	850

25

30

Example 5-8 and Comparative Examples F-GHigh temperature cross-linking of NBR/PA with Perkadox[®] 30: Effects of coagents

TABLE 3

Example	F	G	5	6	7	8
Compound (wt.pts)						
PA-6 (Akulon [®] M2230)	40	40	40	40	40	40
NBR (Krynac [®] 2980)	60	60	60	60	60	60
Perkadox [®] 30	--	--	4	4	4	4
Perkalink [®] 300	--	--	--	2	--	--
Oligomer (m-DIPB)	--	--	--	--	2	--
HVA-2 [®]	--	1	--	--	--	2
Permanax [®] TQ	--	1	--	1	1	1
Mechanical Properties:						
Tensile Strength (MPa)	13.3	16.1	24.2	27.2	29.4	23.8
Modulus 100% (MPa)	13.1	15.5	23.6	27.1	24.9	----
Elongation at break (%)	105	115	102	97	123	69

Results from experiments with NBR and PA-6 showed that a C-C initiator (Perkadox 30), thermoplastic material with better mechanical properties could be obtained than by using only HVA-2[®] (see Example D). Addition of coagents such as Perkalink[®] 300 and an oligo(m-DIPB) further improved the tensile properties, while addition of HVA-2[®] had no such effect. The use of the coagents TAC or oligo(m-DIPB) alone gave poor results (not shown).

Examples 9-11 and Comparative Example H-JPolyamides of different viscosity

Properties of NBR/PA blends with different PA-6 types cross-linked with Px 30 are given in Table 4.

TABLE 4

Example	Compound Composition					wt.pts
	H	9	I	10	J	11
NBR (Krynac®2980)	60	60	60	60	60	60
PA-6 (Akulon® M-223)	40	40	--	--	--	--
PA-6 (Akulon® M258)	--	--	40	40	--	--
PA-6 (Akulon®K-136)	--	--	--	--	40	40
Px 30	--	2	--	2	--	2
Properties						
Tensile Strength [MPa]	12	17	14	23	15	23
Elongation [%]	71	46	73	67	94	60

There is no big difference in tensile strength and elongation between the several Polyamides. The samples cross-linked with Px 30 have better properties than the samples without Px 30.

Examples 12-14

Different types of Polyamide

The properties of NBR/PA blends with different PA types are given in Table 5.

TABLE 5

Example	Compound Composition [wt.pts]		
	12	13	14
NBR	60	60	60
(Krynac [®] 2980)			
Polyamide -12	40	---	---
Polyamide -6,6	---	40	40
Permanax [®] TQ	---	---	1
Px 30	2	2	2
Properties			
Tensile Strength [MPa]	13.4	14.2	15.1
Elongation [%]	89	8	15

Table 5 shows that the tensile strengths of blends with different polyamides were similar. The elongation of the blend with polyamide-12 is better than with PA-6 or PA-6,6.

Examples 15-17

NBR with a higher acrylonitrile content (50%) and with another diene rubber

The mechanical properties of the blends are given in Table 6.

TABLE 6

Example	Compound Composition			wt.pts
	15	16	17	
NBR (Krynac®2980)	30	---	60	
BR (Buna® CB10)	30	---	---	
NBR (Krynac®5075)	---	60	---	
PA-6 (Akulon®K-136)	40	40	40	
Px 30	2	2	2	
Properties				
Tensile Strength [MPa]	21	31	23	
Elongation [%]	58	164	60	

Replacement of part of the NBR by BR did not affect the mechanical properties of the blend (Table 6). NBR with higher acrylonitrile content gave better mechanical properties to the blend with PA-6.

These results indicate that various diene-type rubbers or mixtures thereof may be used in dynamic cross-linking with polyamides using Px 30. Additional compatibilization by block-copolymers, reactive polymers or functional coagents also may be applied, if necessary or desirable.

Examples 18-19

The effect of another polymer on the properties.

TABLE 7

Example	18	19
Akulon®K136 (PA-6)	40	40
NBR (Krynac®2980)	60	30
SAN	--	30
Px 30	2	2
TQ	1	1
MVI [cm³/10min]	14	88
Mechanical properties		
Tensile strength [MPa]	33.6	26.2
Elongation at Rupture[%]	150	34
Yield Strength [MPa]	9	25

(Partial) Replacement of NBR with SAN improved the Yield strength.

Examples 20-25 and Comparative Example KDifferent Combinations of Antioxidants and Cross-linkers

TABLE 8

Compound							
Example	K	20	21	22	23	24	25
PA-6	--	--	40	--	--	--	--
(Akulon®-K124)							
PA-6	40	40	--	40	40	40	40
(Akulon®-K136)							
NBR (Krynac®2980)	60	60	60	60	60	60	60
Px30	--	2	2	--	--	2	2
Px58	--	--	--	2	--	--	--
Oligomeric Px30	--	--	--	--	2	--	--
Permanax® TQ	--	--	1	1	1	--	--
Weston® 618	--	--	--	--	--	1	--
Permanax®6PPD	--	--	--	--	--	--	1
MVI [cm ³ /10 min]	4.0	9.7	15	14	16	16	9.2
Mechanical Properties							
Tensile Strength [MPa]	14.9	30.6	25.7	17.3	17.4	18.9	25.6
Elongation at Rupture [%]	146	135	133	91	58	90	135
Yield Strength [MPa]	5	11	10	8	11	--	8

Examples 26-33 - Different NBR/Polyamide Ratios

TABLE 9

Example	26	27	28	29	30	31	32	33
PA-6 Akulon® K136	30	40	50	60	70	70	80	90
NBR (Krynac® 2980)	70	60	50	40	30	30	20	10
Px 30	2	2	2	2	2	1	2	2
Permanax® IQ	1	1	1	1	1	0.5	1	1
MVI [cm ³ /10 min]	4.4	14	27	40	50	52	56	58
Mechanical Properties								
Tensile strength [MPa]	21.4	33.6	30.5	26.6	38.5	29.9	41.0	48.8
Elongation [%]	123	149	113	29	14	6	5	3
Rupture Strength [MPa]	21.3	33.5	30.3	23.3	36.2	28.0	28.3	23.3
Elongation at Rupture [%]	123	150	114	32	16	7	17	13
Yield Strength [MPa]	6	9	16	22	33	26	41	48

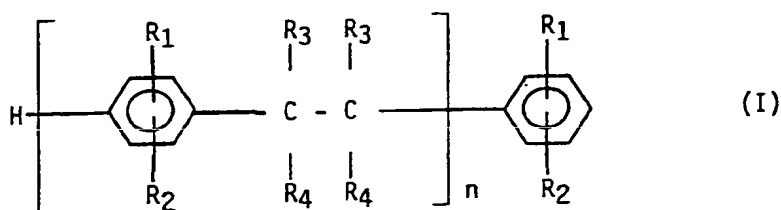
Examples 34-38 - Addition of Plasticizers

TABLE 10

Example	34	35	36	37	38
Akulon® K136 (PA-6)	40	40	40	40	40
Krynac® 2980 (NBR)	60	60	60	60	60
Perkadox® 30	2	2	2	2	2
Permanax® TQ	1	1	1	1	1
DOP	--	10	20	--	--
KF 8	--	--	--	10	20
MVI [cm ³ /min]	6.8	12	7.6	16	25
Tensile Strength [MPa]	21.8	10.9	7.5	15.3	9.8
Elongation [%]	120.5	79	44	139	73

What is claimed is:

1. A process for the cross-linking of a polymer composition which comprises a thermoplastic crystalline or amorphous (co)polymer comprising repeating units containing at least one amide group and 10-90 parts by weight, based on the amount of amide (co)polymer, of an unsaturated natural or synthetic rubber, characterized in that said polymer composition is heated to a temperature above the melting point of said amide (co)polymer and an initiator selected from oligomers of triisopropyl benzene, 1-isopropyl naphthalene dimer, 2-isopropyl naphthalene dimer and initiators represented by the formula I:



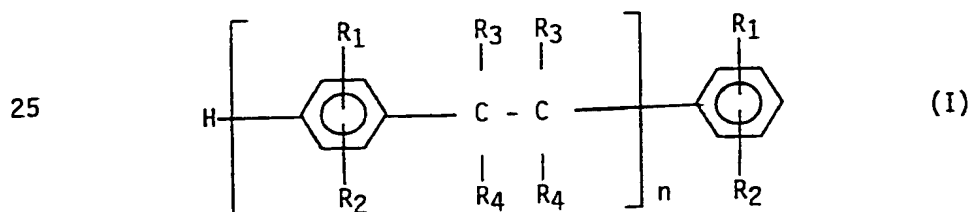
wherein R_1 and R_2 are independently selected from hydrogen, linear or branched $\text{C}_1\text{-C}_{10}$ alkyl and $\text{C}_2\text{-C}_{10}$ alkenyl groups, which may be optionally substituted with one or more halogen atoms, chlorine, $-\text{C}(\text{O})\text{OR}$ and C-O-R ; wherein R is hydrogen or a $\text{C}_1\text{-C}_{10}$ alkyl group;

R_3 and R_4 are independently selected from $-\text{C}\equiv\text{N}$, $-\text{COOH}$, $-\text{OCH}_3$, $-\text{OH}$ and linear or branched $\text{C}_1\text{-C}_{10}$ alkyl, $\text{C}_2\text{-C}_{10}$ alkenyl and aryl groups, which may be optionally substituted with one or more halogen atoms, chlorine, C-O-R and $-\text{C}(\text{O})\text{OR}$; wherein R is a $\text{C}_1\text{-C}_{10}$ alkyl group; and $n=1\text{-}100$; is added with mixing to the heated polymer composition to thereby cross link the polymer composition.

2. A process according to claim 1 wherein the amount of said initiator used in the process is 0.1 to 10.0 weight percent, based on the weight of the unsaturated rubber.
- 5 3. A process according to any one of claims 1-2 wherein said unsaturated rubber is selected from poly(butadiene), poly(isoprene), natural rubber, poly(cyclopentadiene), poly(methylcyclopentadiene), polychloroprene, partly dehydrochlorinated poly(vinyl chloride), butadiene/styrene copolymer, butadiene/acrylonitrile copolymer, partly hydrogenated
10 butadiene/acrylonitrile copolymer, isoprene/styrene copolymer, isobutylene/isoprene copolymer, acrylonitrile/butadiene/styrene terpolymer, ethylene/propylene/diene terpolymer, isoprene/styrene/acrylonitrile terpolymer, rubbery,
15 non-crystalline copolymers of butadiene or isoprene, mixtures of two or more of these rubbers and mixtures of these rubbers with one or more saturated rubbers.
- 20 4. A process according to any one of claims 1-3 wherein said amide (co)polymer is selected from polycaprolactam, polyhexamethylene-1,4-butyrimide, polyhexamethylenedipamide, polyhexamethyleneazelaamide, polyhexamethylenesadipamide, polyhexamethyleneisophthalamide, polylauryllactam, the polyamide derivative of 11-aminoundecanoic acid and mixtures thereof.
- 25 5. A process according to any one of claims 1-4 wherein said process is carried out in the presence of 0.1 to 5.0 weight percent of a polyunsaturated crosslinking coagent, based on the weight of said rubber.
- 30 6. A process according to claim 5 wherein said polyunsaturated crosslinking coagent is selected from triallylcyanurate, triallylisocyanurate, divinylbenzene, diisopropenylbenzene,

oligomers of diisopropenylbenzene, trimethylolpropane trimethacrylate, ethyleneglycol dimethacrylate and m-phenylene bismaleimide.

- 5 7. A process according to any one of claims 1-6 wherein said initiator is selected from 2,3-dimethyl-2,3-diphenylbutane oligomer of diisopropylbenzene and 3,4-dimethyl-3,4-diphenylhexane.
- 10 8. A process according to any one of claims 1-7 wherein said process is carried out in the presence of an effective amount of at least one antioxidant.
- 15 9. A process according to any one of claims 1-8 wherein said process is carried out in the presence of an effective amount of at least one plasticizer for the polymer composition.
- 20 10. Use of an initiator selected from oligomers of triisopropyl benzene, 1-isopropylnaphthalene dimer, 2-isopropylnaphthalene dimer and initiators represented by the formula I:



30 wherein R_1 and R_2 are independently selected from hydrogen, linear or branched C_1 - C_{10} alkyl and C_2 - C_{10} alkenyl groups, which may be optionally substituted with one or more halogen atoms, chlorine, $-\text{C}(\text{O})\text{OR}$ and $-\text{C}-\text{O}-\text{R}$; wherein R is hydrogen or a C_1 - C_{10} alkyl group;

R₃ and R₄ are independently selected from -C≡N, -OCH₃, -COOH, -OH and linear or branched C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl and aryl groups, which may be optionally substituted with one or more halogen atoms, chlorine, -C-O-R and -C(O)OR; wherein R is a C₁-C₁₀ alkyl group; and n=1-100;

to cross-link a polymer composition which comprises a thermoplastic crystalline or amorphous (co)polymer comprising repeating units containing at least one amide group and 10-90 parts by weight, based on the amount of amide (co)polymer, of an unsaturated natural or synthetic rubber, by addition of said initiator with mixing to said polymer composition at a temperature above the melting point of the amide (co)polymer.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 92/02778

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08K5/01; C08L21/00; C08L77/00; //(C08L21/00,77:00)(C08L77/00,21:00)		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08K ; C08L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB,A,1 053 651 (RAYCHEM U.K. LIMITED) 4 January 1967 see claims 10,14-16 see page 2, line 70 - line 75 ---	1
Y	US,A,4 173 556 (A.Y. CORAN ET AL.) 6 November 1979 cited in the application see claim 1 see column 7, line 36 - line 38 ---	1-10
Y	PATENT ABSTRACTS OF JAPAN vol. 14, no. 334 (C-742)(4277) 18 July 1990 & JP,A,21 23 164 (NIPPON PETROLEUM CO LTD) 10 May 1990 cited in the application see abstract ---	1-10
-/--		
<p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
03 MARCH 1993	22. 03. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	VAN HUMBEECK F.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category ^a	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 389 076 (NIPPON OIL CO LTD) 26 September 1990 see claims 1,5,11,13 ---	1,6
A	EP,A,0 430 092 (NIPPON OIL CO LTD) 5 June 1991 see claims 1,6,9 -----	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9202778
SA 67754

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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03/03/93

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EP-A-0389076	26-09-90	JP-A- 2247237 US-A- 5118763	03-10-90 02-06-92
EP-A-0430092	05-06-91	None	